



Synergetic effect of Ni(OH)₂ cocatalyst and CNT for high hydrogen generation on CdS quantum dot sensitized TiO₂ photocatalyst

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ABSTRACT

TiO₂-Ni(OH)₂/CNT/CdS hybrid photocatalyst have been fabricated by a facile synthesis method under room temperature. CdS sensitized TiO₂ hybrid photocatalysts with Ni(OH)₂ and CNT cocatalysts anchored on TiO₂ surface caused significant enhancement in photocatalytic H₂ production rate in lactic acid aqueous solution under visible light irradiation. The optimized TiO₂-Ni(OH)₂/CNT/CdS shows high photocatalytic activity in H₂ generation of 12 mmol g⁻¹ h⁻¹ exceeding TiO₂-Ni(OH)₂/CdS and TiO₂/CNT/CdS which can be attributed to the combined effect of Ni(OH)₂ and CNT. Photoluminescence and photoelectrochemical characteristics results demonstrated that the introduction of Ni(OH)₂ and CNT displays synergetic effect in promoting the separation efficiency of the photoinduced electron-hole pairs. A scheme of charge transfer over the hybrid photocatalyst is proposed indicating the synergetic effect of Ni(OH)₂ and CNT on promoting electron transport at the heterojunction surface between TiO₂ and CdS. The performance of the stability of the TiO₂-Ni(OH)₂/CNT/CdS was tested in the presence of lactic acid under visible light irradiation. The system gives no loss in the hydrogen production after several recycling experiments confirming that the composite is stable and anti-photocorroded.

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1. Introduction

Utilizing the solar resource in water splitting on semiconductor photocatalysts under visible light irradiation is an attractive environmental-friendly way to obtain clean hydrogen energy [1–3]. Considerable efforts have been focused on preparing efficient photocatalysts. Among the various semiconductors, TiO₂ has received widely attention, because of its availability, nontoxicity, low cost, and stability against corrosion [4,5]. However, the photocatalytic ability is limited to UV region because of its wide band gap. To make use of the abundant visible light accounting for about 43% of the solar spectrum, appealing strategy is fabricating heterojunction materials by coupling of effective narrow band gap visible light driven semiconductors such as CdS, NiS, MoS₂ with TiO₂ [6–9]. Our previous work demonstrated that CdS combined with TiO₂ was an efficient catalyst for H₂ production [10]. Sargent reported that CdS quantum dot-sensitized solar cells exhibited energy conversion achieving at 7% [11]. Inorganic narrow gap semiconductor quantum dots (QDs) sensitized TiO₂ systems have a great potential in improving photocatalytic activity. In comparison with common

semiconductor materials, quantum confined semiconductor dots acting as photosensitizers usually display some favorable advantages for photocatalytic hydrogen evolution in aqueous solution due to their excellent light absorption, more active sites, multiple excitons and long exciton lifetimes [12,13]. CdS QDs are dispersed uniformly on the surface of the TiO₂ support avoiding the aggregation of CdS quantum dots and providing with more active sites which is important in improving photocatalytic activity.

It is well known that the photogenerated electrons and holes recombine easily without loading cocatalyst on the semiconductors [14–17]. However, most cocatalysts of noble metals are scarce and expensive for practical applications [18,19]. Therefore, recently intensive studies on earth abundant nickel-based cocatalyst loaded on CdS in photocatalytic hydrogen production have been reported [20–23]. Further more, low-dimensional carbon nanomaterials possessing excellent photoelectron conducting properties can provide direct pathways for charge transport [24–27]. When combined with TiO₂-Ni(OH)₂/CdS heterojunctions, CNT can act as an electron shuttle inducing electron transfer from the conduction band of the CdS to TiO₂-Ni(OH)₂. Herein, we construct CdS sensitized TiO₂ hybrid photocatalysts with Ni(OH)₂ and CNT cocatalysts anchored on TiO₂ surface and their enhancing H₂ generation activity has been investigated in this research. This visible light responsive photocatalytic system is expected to provide some inspirations

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on fabricating photocatalysts composites in improving solar-to-hydrogen efficiency.

2. Experimental section

2.1. Synthesis of $\text{TiO}_2\text{-Ni(OH)}_2$

All the reagents including NaOH, $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, CNTs (purchased from Tsinghua University of China), CdCl_2 , $\text{NH}_3 \cdot \text{H}_2\text{O}$, NH_4Cl , NH_2CSNH_2 and lactic acid were used without further purification. Degussa P25 was used as the source of TiO_2 . 1.0 g P25 was dispersed in 50 mL 1.0 M NaOH aqueous solution and then a calculated amount of $\text{Ni(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in 5 mL H_2O was added, and the solution was stirred for 24 h at room temperature. Then the mixture was centrifuged, washed and dried in vacuum at 353 K for 24 h. The molar ratios of Ni(OH)_2 to $\text{Ni(OH)}_2/\text{TiO}_2$ were 0%, 0.5%, 1%, 2% and 100% respectively.

2.2. Synthesis of $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$

CNT was treated before use. 1 g CNT was dispersed in 100 mL HNO_3 and stirred for 12 h, washed and dried in vacuum at 333 K for 12 h. After that the acidified CNT was suspended in water for further use. 0.1 g $\text{Ni(OH)}_2/\text{TiO}_2$ photocatalyst was dispersed and stirred in a certain volume of 1 mg/mL CNT aqueous solution and then 10 mL 0.08 M CdCl_2 , 10 mL 0.264 M NH_4Cl , 10 mL 0.56 M NH_2CSNH_2 and 10 mL 0.92 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ were added into the mixture in sequence. After stirred for 2 h at room temperature, the trace amount of CdS QDs sensitized $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}$ was centrifuged washed and dried at 333 K in vacuum for 12 h. For comparison, different amount of CdS contained in the composites were also synthesized. $\text{TiO}_2\text{-Ni(OH)}_2/\text{CdS}$ and $\text{TiO}_2/\text{CNT}/\text{CdS}$ were also prepared without adding Ni(OH)_2 or CNT under the same experimental conditions.

3. Characterization

Transmission electron microscopy images were investigated on a high-resolution transmission electron microscopy (JEM-2100, 200 kV). X-ray diffraction (XRD) was performed using a Bruker D8 Advance X-ray powder diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation. The morphologies of the photocatalysts were investigated through field emission scanning electron microscopy (JSM-7001F, operated at 10 kV). Fourier transform infrared (FTIR) spectroscopy was performed with a Nicolet Magna-IR 550-II spectrometer, using KBr pellets. Raman spectra were recorded on a LABRAM-HR in a pulse laser with an excitation wavelength of 514 nm. UV-vis absorption spectroscopy was analyzed using a Shimadzu UV-3600 UV-vis-NIR spectrophotometer at room temperature. BaSO_4 was used as the reflectance standard. Photoluminescence was measured on a fluorescence spectrometer (F-7000, Hitachi, Japan). The time resolved fluorescence decay spectra were obtained on a steady state and time resolved fluorescence spectrometers (FLSP920). X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo ESCALAB 250 XPS spectrometer. The effect of sample surface charging was eliminated by shifting the XPS peak of carbon C1 s to 284.8 eV.

3.1. Photocatalytic measurements

Photocatalytic reactions were carried out in a flowing system (Ar gas with a flow rate at 1.5 L/h) with an inner-irradiation-type Pyrex reactor and a 300 W Xenon arc light source after filtering the UV light using a quartz water jacket filling with circulating cooling NaNO_2 aqueous solution (1 M) to pass only visible light ($\lambda > 400 \text{ nm}$). Recycling NaNO_2 solution was also utilized to main-

tain a constant reactor temperature at 298 K. 50 mg photocatalyst was suspended in 230 mL lactic acid aqueous solution (20 mL lactic acid, 210 mL water). Prior to irradiation, the reactor was purged with Ar gas for 25 min in order to replace air inside the solution. 1 mL of gas was sampled intermittently from the flowing system and then the amount of H_2 evolved was analyzed by gas chromatography (Beifen-Ruili: SP-2100, MS-5A column, TCD, Ar carrier).

3.2. Electrochemical measurements

Photocurrent measurements were performed on an electrochemical workstation (CHI 660D Shanghai, China) using a standard three-electrode system with prepared samples as working electrode, a Pt foil as counter electrode and a standard calomel electrode in saturated KCl as reference electrode. The electrolyte was an aqueous solution containing 0.25 mM Na_2S and 0.25 mM Na_2SO_3 . The working electrode were prepared as follows: photocatalyst (0.1 g) was stirred with 3 mL isopropyl alcohol for 24 h to form a slurry, and then the slurry was spin-coated onto FTO glass for further investigation.

4. Results and discussion

Fig. 1a shows the morphology of $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$ photocatalyst. It can be clearly seen that TiO_2 have an average diameter of 25 nm and small particles of CdS quantum dots with diameter about 5 nm closely adjacent to TiO_2 particles (Fig. 1b). Especially, the doped CNT were distributed uniformly on the surface of the particles. However, the cocatalyst of Ni(OH)_2 cluster were not found in the system. It can be ascribed to the primary crystal nucleus without ripening process to form regular particles. TEM images of the photocatalyst show that TiO_2 , CdS and Ni(OH)_2 are interacted with each other closely to form a composite.

X-ray photoelectron spectroscopy was employed to analyze the chemical composition of the photocatalyst. As shown in Fig. 1c, it is clear that the typical Cd3d peaks at 405.2 and 411.9 eV and S2p peaks at 161.5 and 162.7 eV corresponded to the CdS. The C1 s peak at 284.6 eV mainly ascribed to the CNT added in the photocatalyst. The peaks of Ti2p located at about 459.0 and 464.4 eV implying in the form of TiO_2 were also observed. Fig. 1d also shows the Ni2p signals observed at 856.1 and 874.0 eV, implying that the status of Ni element are major Ni^{2+} in Ni(OH)_2 compounds.

Fig. 2a shows the XRD patterns of the $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$ with different CdS contents. All samples exhibit the same characteristic diffraction peaks correspond to the TiO_2 (JCPDS card no. 21-1272) and CdS (JCPDS card no. 41-1049). It is noteworthy that the typical diffraction peaks assigned to CNT can hardly be identified which could be ascribed to the main peak of CNTs at 25° is overlapped with the peak of TiO_2 . The SEM image and corresponding SEM-EDX mapping (Fig. 2b and c) demonstrated the presence of Ti, O, Cd, S, C and Ni in the composite, and these elements are all well dispersed.

To confirm the composition of the composite and the interaction between TiO_2 , CdS and CNT, FTIR spectra of the catalysts were compared in Fig. 3a. All the samples displayed the broad absorption at 3400 cm^{-1} and 1624 cm^{-1} , which is related to the bending vibrations of adsorbed water molecules. By comparing the composite with TiO_2 , CdS, the two new peaks centered at 1010 cm^{-1} and 1396 cm^{-1} can be ascribed to the newly formed Ti-O-C [28,29] and C-S [30], respectively. The results indicated an evident chemical bond link between TiO_2 and CNT, CdS and CNT.

Raman spectroscopy has also been employed to further provide structure information of the composite as shown in Fig. 3b. Prominent band at 293 cm^{-1} , 589 cm^{-1} and 881 cm^{-1} corresponding to CdS strongly indicated the CdS quantum dots were highly dispersed

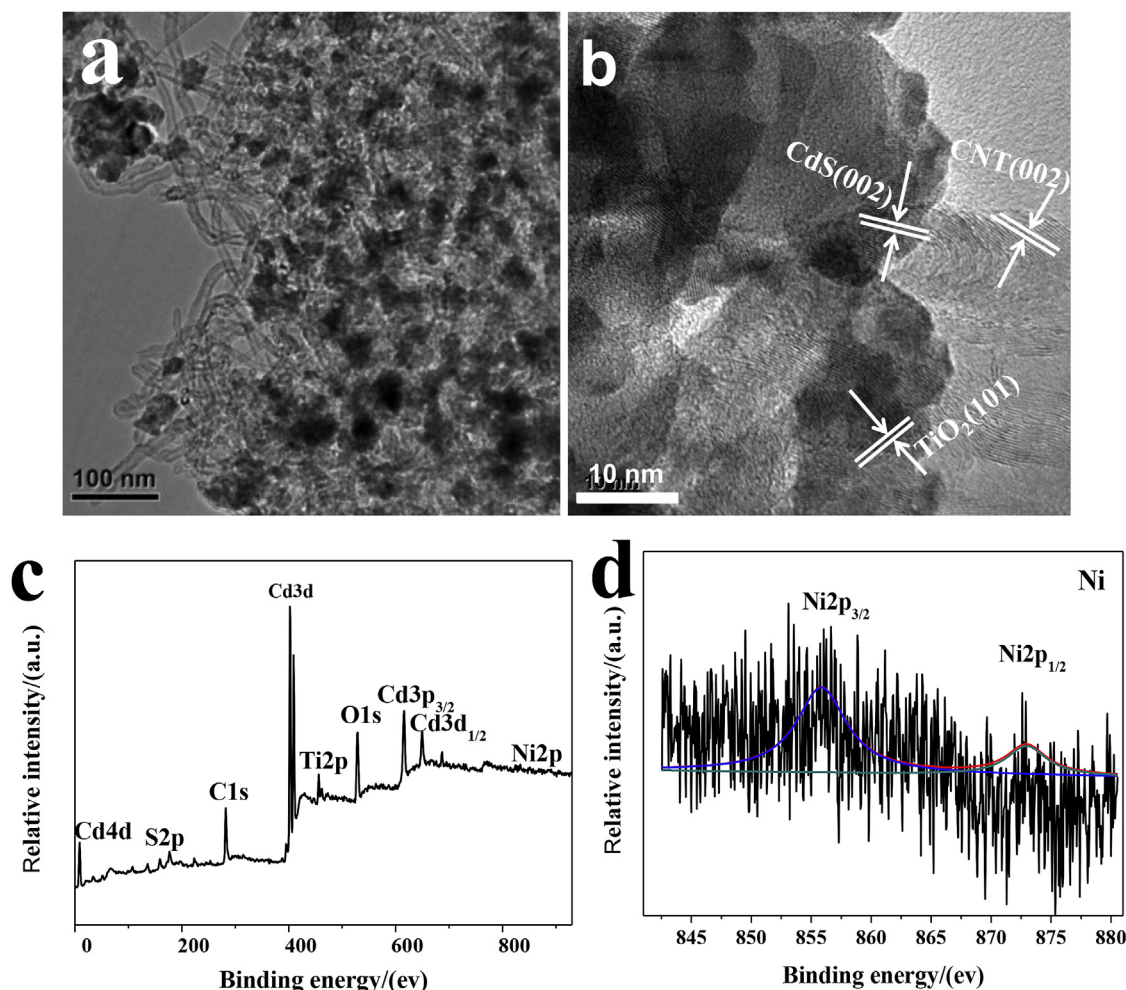


Fig. 1. TEM images of $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$ (a,b) and XPS survey spectra of $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$ and Ni 2p(c,d).

on the external surface of the composite. Compared with TiO_2 and CNT, the vibration peak of 144 cm^{-1} correspond to the TiO_2 vibration mode, the D peak at 1350 cm^{-1} and the G peak at 1570 cm^{-1} all weakened, which is believed to derive from the CdS coating. The peak at 1100 cm^{-1} can be attributed to the vibration of Ni(OH)_2 [31].

The comparison of UV–vis diffuse reflectance spectra of TiO_2 , CdS, TiO_2/CdS , $\text{TiO}_2\text{-Ni(OH)}_2/\text{CdS}$, $\text{TiO}_2/\text{CNT}/\text{CdS}$ and $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$ is displayed in Fig. 4. It is obviously that the absorption edges of pure TiO_2 and CdS are estimated to be 370 nm and 517 nm respectively. After doped with Ni(OH)_2 and CNT, no clear shift of the absorption edge for $\text{TiO}_2\text{-Ni(OH)}_2/\text{CdS}$, $\text{TiO}_2/\text{CNT}/\text{CdS}$ and $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$ was observed in comparison to TiO_2/CdS , implying that Ni(OH)_2 and CNT were not doped into the crystal structure of TiO_2 and CdS. The result shows that Ni(OH)_2 and CNT has no effect on optical properties of TiO_2/CdS . To ensure whether the Ni(OH)_2 and CNT have any effect on photocatalytic activity, we conducted the H_2 generation experiment.

Catalysts with different amount of CdS were firstly tested to evaluate the photocatalytic activity (Fig. S1). The H_2 evolution rate of 10 wt% CdS loaded composite is higher than all other ones (5 wt%, 20 wt% and 40 wt% CdS). Control experiments were also conducted to investigate the effect of the amount of Ni(OH)_2 and CNT on the photocatalytic H_2 production activity. Pure Ni(OH)_2 and CNT were used for comparison, no hydrogen were detected (Fig. 5). As shown in Fig. 5a, in the absence of Ni(OH)_2 , the H_2 production rate was $1.01\text{ mmol g}^{-1}\text{ h}^{-1}$, after loading with a small amount

of Ni(OH)_2 , the H_2 production rate was significantly enhanced to $8.65\text{ mmol g}^{-1}\text{ h}^{-1}$ (0.5 wt%), about 9 times higher than the aforementioned sample. When the content was 1 wt%, the H_2 production rate reached to the highest value of about $12\text{ mmol g}^{-1}\text{ h}^{-1}$. Further increasing amount to 2 wt% Ni(OH)_2 , however, the H_2 generation rate decreased to $7.56\text{ mmol g}^{-1}\text{ h}^{-1}$. A series of the $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$ compounds with different doping amounts of CNT were also compared for the H_2 production (Fig. 5b). For $\text{TiO}_2\text{-Ni(OH)}_2/\text{CdS}$ catalyst without CNT, photocatalytic H_2 production rate was $5.36\text{ mmol g}^{-1}\text{ h}^{-1}$. It was observed that the H_2 generation rate increased with increasing doping amount of CNT. The highest H_2 generation rate of $12\text{ mmol g}^{-1}\text{ h}^{-1}$ was achieved at the amount of 4% CNT, further increasing the CNT amount led to a decrease of the H_2 production. This can be ascribed to the shielding effect [32] in the presence of a large percentage of carbon materials.

To investigate the role of CNT and Ni(OH)_2 for enhanced photocatalytic activity, H_2 generation were compared as shown in Fig. 6a. The rate of H_2 generation of $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$ reaches to about $12\text{ mmol g}^{-1}\text{ h}^{-1}$, while for these in the absence of Ni(OH)_2 or both CNT and Ni(OH)_2 , the H_2 evolution rate were decreased to $5.36\text{ mmol g}^{-1}\text{ h}^{-1}$ and $0.57\text{ mmol g}^{-1}\text{ h}^{-1}$ respectively, which is much lower than that of $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$, indicating that Ni(OH)_2 is an excellent cocatalyst for promoting highly photocatalytic activity in hydrogen production. It can be seen that after doped with CNT, the hydrogen generation rate of $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$ is about 2 times faster than that for $\text{TiO}_2\text{-Ni(OH)}_2/\text{CdS}$, which can be ascribed to the excellent electrical

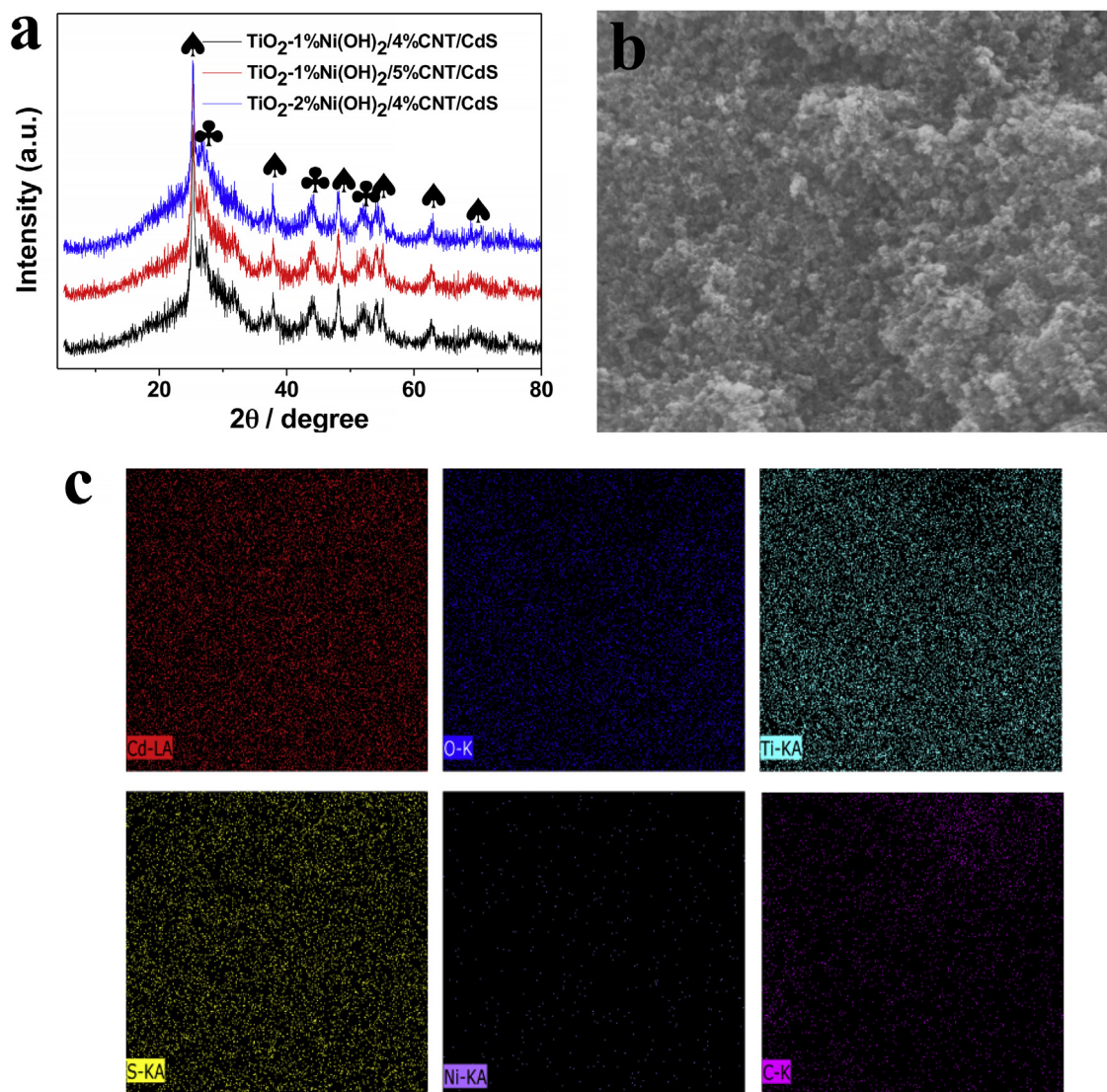


Fig. 2. Comparing XRD patterns of as-prepared optimized $\text{TiO}_2\text{-Ni(OH)}_2\text{/CNT/CdS}$ with various CNT and Ni(OH)_2 content (a); SEM image and corresponding EDX mapping of $\text{TiO}_2\text{-Ni(OH)}_2\text{/CNT/CdS}$ (b, c). ♠- corresponding to TiO_2 , ♣-corresponding to CdS.

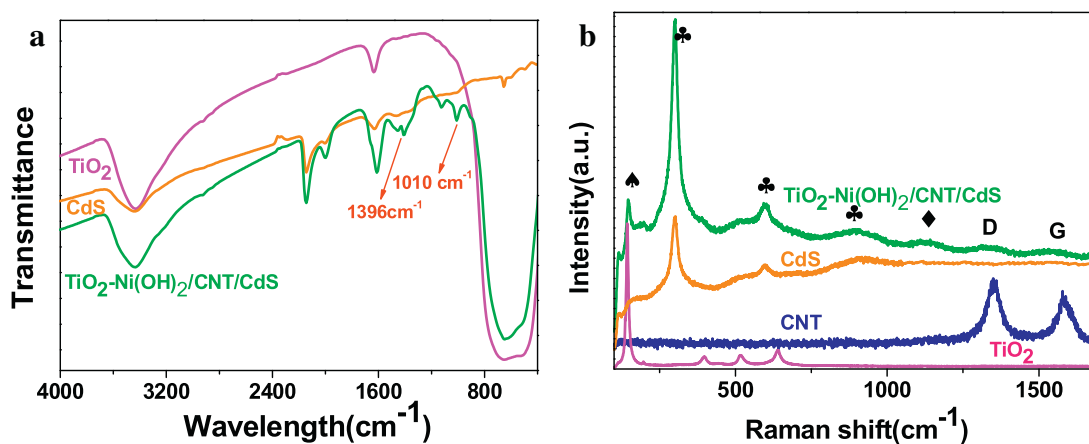


Fig. 3. FTIR spectra of TiO_2 , CdS and $\text{TiO}_2\text{-Ni(OH)}_2\text{/CNT/CdS}$ (a) and Raman spectra of TiO_2 , CdS, CNT and $\text{TiO}_2\text{-Ni(OH)}_2\text{/CNT/CdS}$ (b). ♠- corresponding to TiO_2 , ♣-corresponding to CdS, ♦ – corresponding to Ni(OH)_2 .

conductivity of CNT, facilitating efficient charge carriers transport. To evaluate the stability of $\text{TiO}_2\text{-Ni(OH)}_2\text{/CNT/CdS}$ photocatalyst,

recycling test was performed. As shown in Fig. 7, no significant decrease of H_2 production is observed after 5 cycling, which

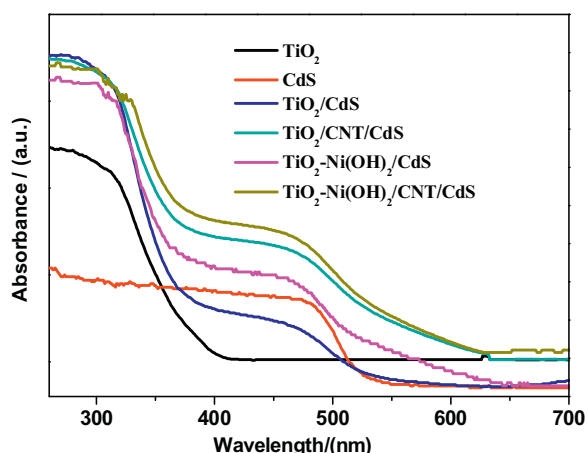


Fig. 4. UV-vis spectra of TiO_2 , CdS, TiO_2/CdS , $\text{TiO}_2\text{-Ni(OH)}_2/\text{CdS}$, $\text{TiO}_2/\text{CNT}/\text{CdS}$ and $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$.

indicates the good stability of $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$ against photocorrosion. After the stability test, the composite was collected and further characterized by XRD, XPS and TEM as shown in Fig. S2, and all results give no obvious changes compared with that from the original catalysts.

To further verify the reason for high photoactivity, the transient photocurrent response of the samples were investigated and shown in Fig. 6b. It was clear that the $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$ electrode exhibited higher photocurrent density than TiO_2/CdS and $\text{TiO}_2\text{-Ni(OH)}_2/\text{CdS}$, which indicates that by doping CNT and loading Ni(OH)_2 cocatalyst, the recombination of electron-hole pairs is suppressed. Especially for the TiO_2/CdS catalyst without loading cocatalyst of Ni(OH)_2 and CNT exhibits a drastically decreasing photocurrent density because of the rapid recombination of the photoinduced electrons and holes.

Photoluminescence spectra and time resolved photoluminescence spectra were used to explain the photogenerated carriers transfer process. Fig. 6c shows the PL spectrum, with emission bands at about 595 nm, compared with TiO_2/CdS , unloaded cocatalysts and CNT, emission intensity of $\text{TiO}_2\text{-Ni(OH)}_2/\text{CdS}$ and $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$ were drastically quenched after loading with Ni(OH)_2 , indicating that Ni(OH)_2 are very efficient traps for electrons photoinduced from CdS to TiO_2 , which simultaneously suppresses the charge recombination process and enhance the photocatalytic activity. CNT provides pathway for the fluent electron transport, also suppressing the recombination of elec-

Table 1

Biexponential decay parameters for emission decay of TiO_2/CdS , $\text{TiO}_2\text{-Ni(OH)}_2/\text{CdS}$, and $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$.

Samples	a1	$\tau_1(\text{ns})$	a2	$\tau_2(\text{ns})$	$\langle\tau\rangle(\text{ns})$
$\text{TiO}_2/\text{CNT}/\text{CdS}$	0.2564	0.418	0.0158	3.279	1.62
$\text{TiO}_2\text{-(Ni(OH)}_2\text{)CdS}$	0.6282	0.216	0.0040	4.649	1.10
$\text{TiO}_2\text{-(Ni(OH)}_2\text{)}/\text{CNT}/\text{CdS}$	0.7029	0.201	0.0021	4.113	0.87

tron hole pairs [33]. Time resolved photoluminescence spectra for the samples provides a tool to evaluate their performance for electron-hole separation. As shown in Fig. 6d, the lifetime of TiO_2/CdS , $\text{TiO}_2\text{-Ni(OH)}_2/\text{CdS}$ and $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$ is compared, and the average decay lifetimes are 1.62 ns, 1.10 ns and 0.87 ns respectively (Table 1). The lifetime of $\text{TiO}_2\text{-Ni(OH)}_2/\text{CdS}$ and $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$ is much shorter than that of TiO_2/CdS , indicating the effective charge transfer from CdS to Ni(OH)_2 . The results demonstrated that Ni(OH)_2 as an effective cocatalyst fixed on TiO_2 significantly improve the charge injection from CdS to TiO_2 , and ultimately into Ni(OH)_2 . As compared to $\text{TiO}_2\text{-Ni(OH)}_2/\text{CdS}$, the lifetime of $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$ gives no noticeable decrease. These indicate that CNT in the hybrids has little influence on the rate of charge injection process, however, it may play an important role in improving the charge separation, that is the CNT suppress the back electron transfer between the injected electrons in Ni(OH)_2 and the holes in CdS [34]. This contributes to the better photocatalytic activity for hydrogen generation, from 5.36 to 11.87 $\text{mmol g}^{-1} \text{h}^{-1}$ (Fig. 6a).

Schematic illustration of the synergetic effect of Ni(OH)_2 and CNT on enhanced photocatalytic H_2 production activity mechanism for $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$ hybrid is shown in Fig. 8. Visible light irradiation excited the electrons of the supported CdS QDs from the VB to CB. Then the electrons will be attracted immediately to the deposited Ni(OH)_2 on TiO_2 surface pass through CNT, and holes left to react with sacrificial agents of $\text{Na}_2\text{S}/\text{Na}_2\text{SO}_3$. The charge carrier separation was enhanced attributing to the excellent conductivity of CNT acting as a superhighway for the transport of the photogenerated electrons. Electrons trapped by Ni(OH)_2 cocatalyst as the active reaction sites facilitated the reduction process of proton to hydrogen.

5. Conclusion

Simple and facile liquid chemistry synthetic method under room temperature was applied to prepare $\text{TiO}_2\text{-Ni(OH)}_2/\text{CNT}/\text{CdS}$ hybrid photocatalyst. The photocatalytic H_2 production performance of the typical CdS QDs sensitized TiO_2 -based system was

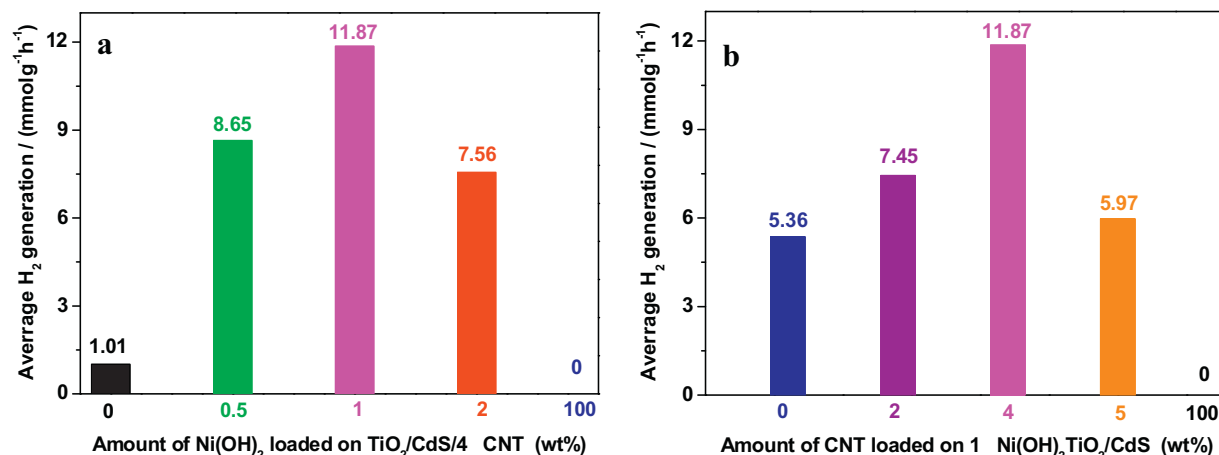


Fig. 5. Comparison of the photocatalytic activity of $\text{TiO}_2\text{-Ni(OH)}_2/\text{CdS}$ under different conditions.

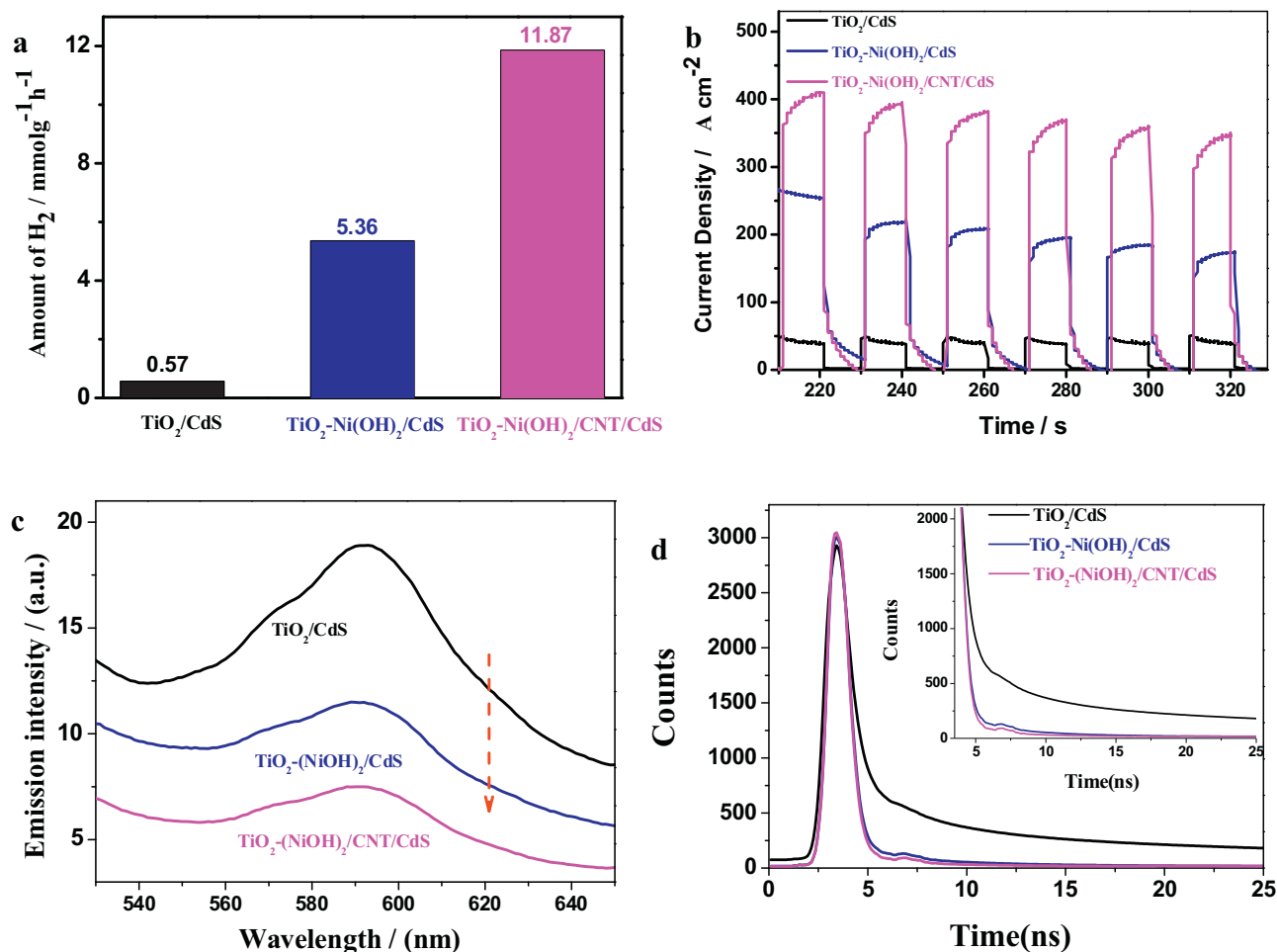


Fig. 6. (a) Comparison of the H_2 evolution activity of the $TiO_2/CNT/CdS$ with $TiO_2-Ni(OH)_2/CdS$, and $TiO_2-Ni(OH)_2/CNT/CdS$, in which the amount of CNT and $Ni(OH)_2$ is optimized to 1 wt% and 4 wt% respectively. Light source 300 W Xe lamp ($\lambda > 400\ nm$). Reaction solution: 0.1 M $Na_2S-Na_2SO_3$ in 230 mL deionized water, Cat. 0.05 g. (b) Photocurrent response in Na_2S/Na_2SO_3 aqueous solution with on-off visible light illumination ($100\ mW\ cm^{-2}$) at 0.0 V vs NHE. (c) Photoluminescence spectra of $TiO_2/CNT/CdS$, $TiO_2-Ni(OH)_2/CdS$, and $TiO_2-Ni(OH)_2/CNT/CdS$. (d) Time resolved PL emission decay of $TiO_2/CNT/CdS$, $TiO_2-Ni(OH)_2/CdS$, and $TiO_2-Ni(OH)_2/CNT/CdS$ (curves represent the kinetic fit using biexponential decay analysis) with an excitation wavelength of 450 nm.

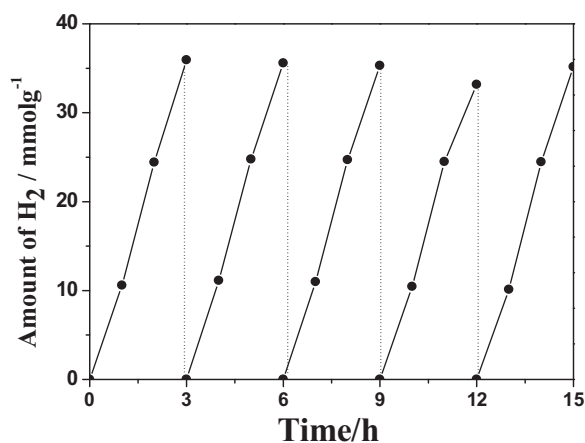


Fig. 7. Cycle test on $TiO_2-Ni(OH)_2/CNT/CdS$ suspended in 230 mL 0.1 M Na_2S/Na_2SO_3 aqueous solution bubbled with Ar per 3 h under irradiation of visible light.

promoted for the first time by the synergetic effect of $Ni(OH)_2$ and CNT. The optimized photocatalytic activity is achieved over $TiO_2-Ni(OH)_2/CNT/CdS$ with a rate of $12\ mmol\ g^{-1}\ h^{-1}$. The excellent photocatalytic performance is mainly attributed to the facilitated charge separation and transfer at the interface of heterojunction

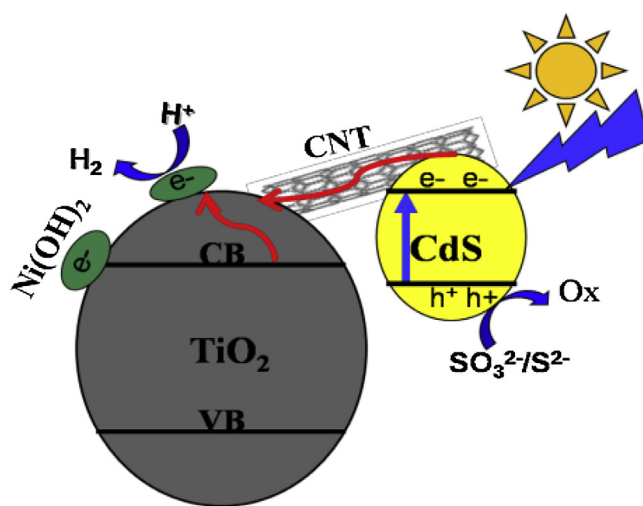


Fig. 8. Schematic illustration of the charge separation and electron transfer in the $TiO_2-Ni(OH)_2/CNT/CdS$ system under visible light irradiation.

construction between TiO_2 and CdS via coefficient effect of $Ni(OH)_2$ and CNT.

In particular, the photocatalyst composition shows good stability and anti-photocorrosion under visible-light irradiation. The facile and environmentally synthesis technique can provide a way to produce other high catalytic H_2 generation via deposited with non-noble cocatalyst and doped with nanocarbon charge transfer materials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.12.008>.

References

- [1] Y.P. Yuan, L.W. Ruan, J. Barber, et al., Hetero-nanostructured suspended photocatalysts for solar-to-fuel conversion, *Energy Environ. Sci.* 7 (12) (2014) 3934–3951.
- [2] X. Li, J. Yu, J. Low, et al., Engineering heterogeneous semiconductors for solar water splitting, *J. Mater. Chem. A* 3 (6) (2014) 2485–2534.
- [3] J. Ran, J. Zhang, J. Yu, et al., ChemInform abstract: earth-abundant cocatalysts for semiconductor-based photocatalytic water splitting, *Chem. Soc. Rev.* 43 (22) (2014) 7787–7812.
- [4] Y. Ma, X. Wang, Y. Jia, et al., Titanium dioxide-based nanomaterials for photocatalytic fuel generations, *Chem. Rev.* 114 (19) (2014) 9987–10043.
- [5] C. Zhao, H. Luo, F. Chen, et al., A novel composite of TiO_2 nanotubes with remarkably high efficiency for hydrogen production in solar-driven water splitting, *Energy Environ. Sci.* 7 (5) (2014) 1700–1707.
- [6] Y. Zhu, C. Zhi, G. Tong, et al., Construction of hybrid Z-scheme Pt/CdS –TNTAs with enhanced visible-light photocatalytic performance, *Appl. Catal. B: Environ.* 163 (2015) 16–22.
- [7] J. Ran, J. Zhang, J. Yu, et al., Enhanced visible-light photocatalytic H_2 production by $Zn_xCd_{1-x}S$ modified with earth-abundant nickel-based cocatalysts, *Chemosuschem* 7 (12) (2014) 3426–3434.
- [8] C.T. Dinh, M.H. Pham, F. Kleitz, et al., Design of water-soluble CdS –titanate–nickel nanocomposites for photocatalytic hydrogen production under sunlight, *J. Mater. Chem.* 1 (42) (2013) 13308–13313.
- [9] B. Song, L. Wang, et al., Chemically exfoliated metallic MoS_2 nanosheets: a promising supporting co-catalyst for enhancing the photocatalytic performance of TiO_2 nanocrystals, *Nano Res.* 8 (1) (2015) 175–183.
- [10] J. Zhang, Z. Zhu, Y. Tang, et al., Titania nanosheet-mediated construction of a two-dimensional Titania/Cadmium sulfide heterostructure for high hydrogen evolution activity, *Adv. Mater.* 26 (5) (2014) 734–738.
- [11] A.H. Ip, S.M. Thon, S. Hoogland, et al., Hybrid passivated colloidal quantum dot solids, *Nat. Nanotechnol.* 7 (9) (2012) 577–582.
- [12] Y. Pan, T. Zhou, J. Han, et al., CdS quantum dots and tungsten carbide supported on anatase–rutile composite TiO_2 for highly efficient visible-light-driven photocatalytic H_2 evolution from water, *Catal. Sci. Technol.* 6 (7) (2015) 2206–2213.
- [13] Jiu-Ju Wang, Zhi-Jun Li, X.B. Li, et al., Inside cover picture: photocatalytic hydrogen evolution from glycerol and water over nickel-hybrid cadmium sulfide quantum dots under visible-light irradiation, *Chemosuschem* 7 (5) (2014) 1468–1475.
- [14] J. Yang, D. Wang, H. Han, et al., Roles of cocatalysts in photocatalysis and photoelectrocatalysis, *Acc. Chem. Res.* 46 (8) (2013) 1900–1909.
- [15] H. Yu, X. Huang, P. Wang, et al., Enhanced photoinduced-stability and photocatalytic activity of CdS by dual amorphous cocatalysts: synergistic effect of $Ti(IV)$ -hole cocatalyst and $Ni(II)$ -electron cocatalyst, *J. Phys. Chem. C* 120 (7) (2016) 3722–3730.
- [16] X. Zhou, J. Jin, X. Zhu, et al., New $Co(OH)_2/CdS$ nanowires for efficient visible light photocatalytic hydrogen production, *J. Mater. Chem. A* 4 (14) (2016) 5282–5287.
- [17] W. Zhang, Y. Wang, Z. Wang, et al., Highly efficient and noble metal-free NiS/CdS photocatalysts for H_2 evolution from lactic acid sacrificial solution under visible light, *Chem. Commun.* 46 (40) (2010) 7631–7633.
- [18] Lu Q., Yu Y., Ma Q., et al., 2D Transition-Metal-Dichalcogenide-Nanosheet-Based Composites for Photocatalytic and Electrocatalytic Hydrogen Evolution Reactions. 2016, 28, 10, 1917–1933.
- [19] S. Cao, Y. Chen, C.C. Hou, et al., Cobalt phosphide as a highly active non-precious metal cocatalyst for photocatalytic hydrogen production under visible light irradiation, *J. Mater. Chem. A* 3 (11) (2015) 6096–6101.
- [20] X. Yue, S. Yi, R. Wang, et al., Cadmium sulfide and nickel synergetic co-catalysts supported on graphitic carbon nitride for visible-light-driven photocatalytic hydrogen evolution, *Sci. Rep.* 6 (2016) 22268.
- [21] Z. Yan, X. Yu, Y. Zhang, et al., Enhanced visible light-driven hydrogen production from water by a noble-metal-free system containing organic dye-sensitized titanium dioxide loaded with nickel hydroxide as the cocatalyst, *Appl. Catal. B: Environ.* 160–161 (1) (2014) 173–178.
- [22] Z. Sun, H. Zheng, J. Li, et al., Extraordinarily efficient photocatalytic hydrogen evolution in water using semiconductor nanorods integrated with crystalline Ni_2P cocatalysts, *Energy Environ. Sci.* 8 (9) (2015) 2668–2676.
- [23] Z. Chai, T.T. Zeng, L. Qi, et al., Efficient visible light-driven splitting of alcohols into hydrogen and corresponding carbonyl compounds over a Ni-modified CdS photocatalyst[J], *J. Am. Chem. Soc.* 138 (32) (2016) 10128–10131.
- [24] L. Wang, Z. Yao, F. Jia, et al., A facile synthesis of $Zn_xCd_{1-x}S/CNTs$ nanocomposite photocatalyst for H_2 production, *Dalton Trans.* 42 (27) (2013) 9976–9981.
- [25] M. Li, K. Chang, T. Wang, et al., Hierarchical nanowire arrays based on carbon nanotubes and Co_3O_4 decorated ZnO for enhanced photoelectrochemical water oxidation, *J. Mater. Chem. A* 3 (26) (2015) 13731–13737.
- [26] N. Zhang, Y. Zhang, M.Q. Yang, et al., A critical and benchmark comparison on graphene-, carbon nanotube-, and fullerene-semiconductor nanocomposites as visible light photocatalysts for selective oxidation, *J. Catal.* 299 (2) (2013) 210–221.
- [27] N. Zhang, Y. Zhang, Y.J. Xu, Recent progress on graphene-based photocatalysts: current status and future perspectives, *Nanoscale* 4 (19) (2012) 5792–5813.
- [28] S. Wang, S. Zhou, Photodegradation of methyl orange by photocatalyst of $CNTs/P-TiO_2$ under UV and visible-light irradiation[J], *J. Hazard. Mater.* 185 (1) (2011) 77–85.
- [29] U. Caudillo-Flores, J. Lara-Romero, J. Zárate-Medina, et al., Enhanced photocatalytic activity of $MWCNT/TiO_2$, heterojunction photocatalysts obtained by microwave assisted synthesis[J], *Catal. Today* 266 (2016) 102–109.
- [30] C. Zhang, Y. Lu, Q. Jiang, et al., Synthesis of CdS hollow spheres coupled with g-C $_3$ N $_4$ as efficient visible-light-driven photocatalysts[J], *Nanotechnology* 27 (35) (2016) 355402.
- [31] W. Zhou, X. Cao, Z. Zeng, et al., One-step synthesis of Ni_3S_2 nanorod@ $Ni(OH)_2$ nanosheet core-shell nanostructures on a three-dimensional graphene network for high-performance supercapacitors[J], *Energy Environ. Sci.* 6 (7) (2013) 2216–2221.
- [32] Q. Li, B. Guo, J. Yu, et al., Highly efficient visible-light-driven photocatalytic hydrogen production of CdS -cluster-decorated graphene nanosheets, *J. Am. Chem. Soc.* 133 (28) (2011) 10878–10884.
- [33] W.K. Jo, N.C.S. Selvam, Fabrication of photostable ternary $CdS/MoS_2/MWCNTs$ hybrid photocatalysts with enhanced H_2 generation activity, *Appl. Catal. A Gen.* 525 (2016) 9–22.
- [34] P. Brown, A. Kensuke Takechi, P.V. Kamat, Single-walled carbon nanotube scaffolds for dye-sensitized solar cells, *J. Phys. Chem. C* 112 (12) (2008) 4776–4782.